

Detection of Terbium(III) Ions by a Selective Electrode Based on a Hydrazinecarboxamide Derivative

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Solution study showed that N-phenyl-2-(phenylcarbamothioyl) hydrazinecarboxamide (PPH) has a tendency to selectively bind with Tb(III) ions as compared to other tested ions and the data led us to hypothesize that the ligand can be used as an ionophore in construction of terbium ion selective electrodes. Electrode composed of 30% PVC, 65% a solvent mediator (DBP), 3% (PPH) and 2% of an ionic additive (i.e. NaTPB) were found to show the best potentiometric response characteristics with a Nernstian potential response of 19.7 mV per decade over the concentration range 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹. The response time of the electrodes were found to be as short as ~10 s and it was found to work well in the pH range of 2.8-8.5 and was applicable for at least 2 months. The proposed membrane sensor shows excellently discriminates Tb³⁺ ions as compared to several alkali, alkaline earth, transition and heavy metal ion.

Keywords: Sensor, Potentiometry, Ion-Selective, PVC Membrane

1. INTRODUCTION

Calcium fluoride, calcium tungstate and strontium molybdate, used in solid-state devices are doped with terbium and the element is also applied as a crystal stabilizer of fuel [1]. The most important use of the element is in an alloy composed of dysprosium and a little iron called Terfenol which is used in actuators, sonar systems and sensors [2] as well as its use in green phosphors in fluorescent lamps and color TV tubes [3]. Recent applications of the element include its uses as a probing reagent to mapping metal-binding sites on important biological macromolecules due to its similar chemical properties to calcium and magnesium ion [4, 5].

Terbium has a tendency to bind with the same sites on RNA as magnesium, with a much higher affinity⁶ and as well as other lanthanides have found some therapeutic applications. These have shown

it can enhance the cytotoxicity of cisplatin, possibly by increasing accumulation of drug in cisplatin-resistant cells [6] which creates the need for its online monitoring in biological environments.

In general, luminescence of terbium complexes is the bases of many fluorescence labelling in clinical chemistry and molecular biology, due to intramolecular energy transfer through the triplet state of the ligand to the emitting level of the terbium ion [7]. Ion selective electrodes constitute one of the suitable methods for monitoring and determination of rare earth elements, which have become especially interesting due to their advantages of low cost, portability, selectivity, and simple operator. These devices also provide an analysis method without destruction of sample and can be used in complex matrix of samples [8-40].

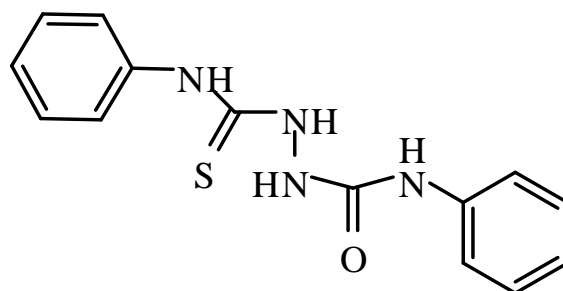


Figure 1. Chemical structure of PPH.

Hence the potentials of N-phenyl-2-(phenylcarbamothioyl) hydrazinecarboxamide (PPH), Fig. 1, as sensing material in the terbium sensor was evaluated based on the studies on its interaction with some metal cations through conductometrically in acetonitrile solution. Due to the verification of the incredible interaction of PPH with terbium ion, the compound was chosen as a terbium selective sensing material to be incorporated in the composition of ion selective membranes.

2. EXPERIMENTAL

2.1. Reagents

Nitrate and chloride salts of all cations and the reagent grades of benzyl acetate (BA), nitrobenzene (NB), acetophenone (AP), dibutyl phthalate (DBP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight (PVC) were purchased from Merck Chemical and Aldrich Co. During the experiments, doubly distilled deionized water was used.

2.2. Preparation of the electrode

Preparing the PVC membranes included thoroughly mixing the desired amounts of the ingredients (PVC, DBP, NaTPB and PPH) in small amounts of tetrahydroforan in a glass dish and then letting the THF. content evaporate to obtain an oily concentrated mixture to be coated on the tips of

Pyrex tube (3-5 mm i.d.), which were then used as the electrodes [41-55] after keeping them at room temperature for about 12 h, filling them with an internal filling solution (1.0×10^{-3} mol L⁻¹ of TbCl₃) and finally conditioned them for 24 h by soaking in a 1.0×10^{-3} mol L⁻¹ terbium chloride. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. The emf measurements

The electrochemical cell used for the emf measurements was

Ag–AgCl | internal solution, 1.0×10^{-3} mol L⁻¹ TbCl₃ | PVC membrane | sample solution | Hg–Hg₂Cl₂, KCl (satd.)

The potential measurements were carried out using Corning ion analyzer with a 250 pH/mV meter for at 25.0 ± 0.1 °C. The emf values were recorded relative to a double-junction saturated calomel electrode (SCE, Philips) with its chamber filled with an ammonium nitrate solution and the activities were calculated according to the Debye–Huckel procedure [56].

3. RESULTS AND DISCUSSIONS

3.1. The potential response

To evaluate the tendency of PPH toward forming complexes with lanthanide cations, its interaction with some lanthanide ions was investigated through conductometry in acetonitrile solution by as describe earlier [60, 61]. The formation constant, K_f , of the complexes showed the formation of a much stronger complex with Tb(III) ions (K_f : 2.4×10^6) in comparison with the other cations tested.

In the light of the results some PPH-based membrane sensor then were then constructed and used for the determination of terbium ion in different samples. The sensors were found to generate a stable response to Tb(III) ion in aqueous solutions while in the case of the other ions tested the potential slope were much lower than the expected Nernstian slopes of 59, 29.5 and 20 mV per decade for the univalent, bivalent and trivalent cations.

3.2. The effect of composition

Composition the nature of the ingredients directly affect the sensitivity and selectivity of any given membrane sensor [57-63]. Accordingly, different aspects of preparation of membranes based on PPH were studied as summarized Table 1.

Solvent polymeric membrane ion-selective electrodes are usually composed of matrix matrices with solvent mediator/PVC ratio of about 2. Polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high enough mobility of their constituents. In this study, a plasticizer/PVC ratio of about 2.2 was found to be the most suitable.

The selectivity and working concentration range of membrane sensors are also affected by the nature and amount of the plasticizer used, due to the influence of the plasticizer on the dielectric

constant of the membrane phase, the mobility of the ionophore molecules and the optimum conformation of ligands [63-65]. The results in Table 1 show among the four different plasticizers used, DBP resulted in sensors with the best sensitivity.

Tests on the optimum content of the ionophore revealed 3% of PPH to be the optimum amount of the ionophore (no. 6).

Table 1. Optimization of the membrane ingredients

Sensor No.	Composition of the membrane (wt.%)				Slope (mV per decade)	Dynamic Linear range (mol L ⁻¹)
	PVC	Plasticizer	PPH	NaTPB		
1	30	DBP, 68	2	0	12.8 ± 0.4	1.0 × 10 ⁻² -1.0 × 10 ⁻⁵
2	30	DBP, 67	2	1	17.4 ± 0.2	1.0 × 10 ⁻² -5.0 × 10 ⁻⁶
3	30	DBP, 66	2	2	18.5 ± 0.5	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
4	30	DBP, 65	2	3	17.8 ± 0.3	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
5	30	DBP, 67	1	2	15.7 ± 0.6	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
6	30	DBP, 65	3	2	19.7 ± 0.5	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
7	30	NB, 66	2	2	16.8 ± 0.4	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
8	30	AP, 66	2	2	18.2 ± 0.3	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶
9	30	BA, 66	2	2	17.1 ± 0.5	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶

The presence of lipophilic anions in the composition of cationic-selective membrane sensors has not only been reported to diminish the ohmic resistance and improve the potential behavior and selectivity but also in poor extraction capacities, it has been found to increase the sensitivity of the membrane electrodes [64-66]. Table 1 shows that in the absence of a proper additive, the sensitivity of the membrane was low (no. 1 with a slope of 12.8 mV per decade), while adding 2% NaTPB greatly enhanced the sensitivity of the sensor considerably (no. 6 with a slope 19.7 mV per decade).

3.3. Calibration graph and statistical data

The optimum time for the membrane electrode to reach to equilibrium in the presence of 1.0 × 10⁻⁴ mol L⁻¹ TbCl₃ was found to be 24 h. The conditioned electrode showed a linear response to the activity of Tb³⁺ ion in the range of 1.0 × 10⁻⁶ to 1.0 × 10⁻² mol L⁻¹ (Fig. 2), with potential response slopes of 19.7 ± 0.5 mV per decade. The detection limit was found to be as low as 5.6 × 10⁻⁷ mol L⁻¹. Finally studies showed that the membrane electrodes could be used for at least 2 months without any measurable divergence in their behaviors.

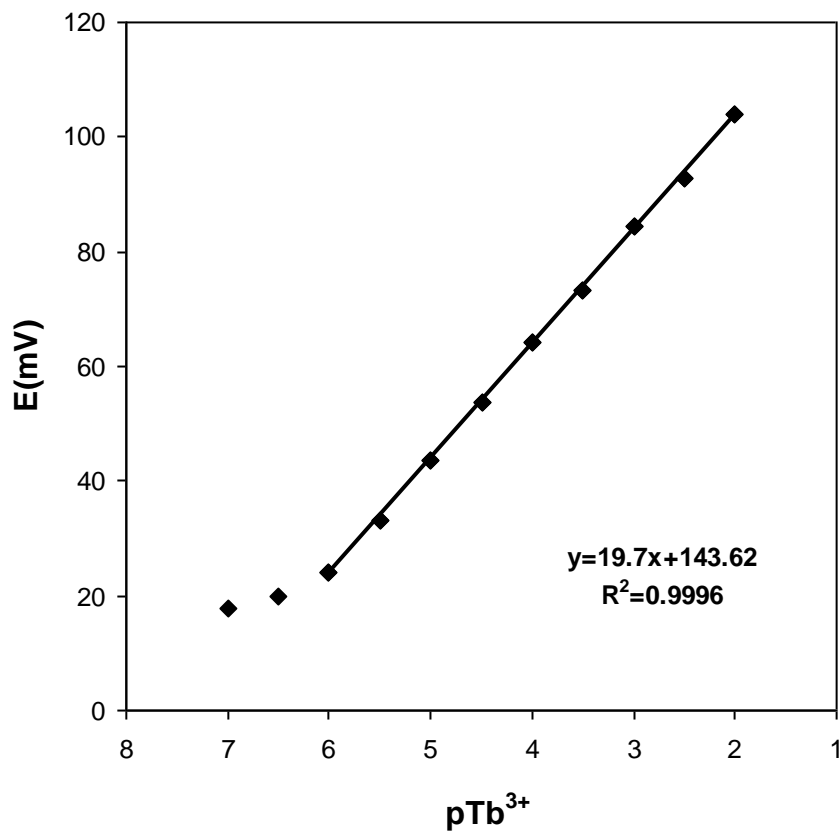


Figure 2. Calibration curve of the terbium electrode based on PPH.

3.4. pH effect and response time

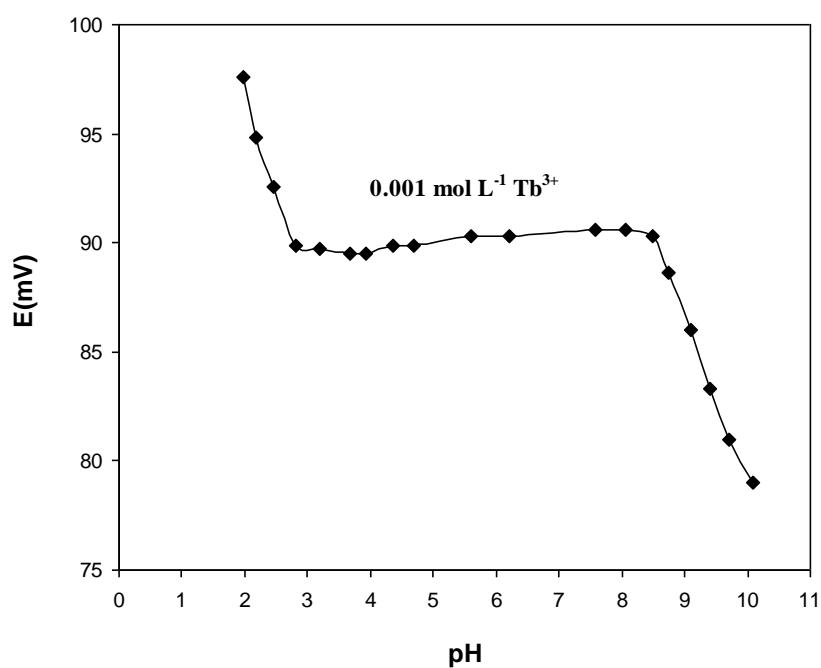


Figure 3. The pH effect of the test solution on the potential response of the terbium sensor (no. 6).

The effect of the test solution pH on the potential response of the sensor was tested in a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ Tb (III) solution over the pH range of 2.0–10.0 and the results are shown in Fig. 3 which shows the electrode response to be independent from solution pH in a range of about 2.8–8.5. At pH values <2.8 the potential response increases irregularly most probably due to the response of the electrode to H_3O^+ ions in solution through the protonation of nitrogen atoms of PPH. The observed potential decreased at $\text{pH} > 8.5$ could be due to the formation of insoluble terbium hydroxide in the solution.

Further the response time of the sensor was recorded by changing the Tb(III) concentration in the test solution in a concentration range of 1.0×10^{-6} to $1.0 \times 10^{-2} \text{ mol L}^{-1}$. The results are shown in Fig. 4 reveal that in the whole concentration range the electrode reached its equilibrium response in about ~ 10 s.

3.5. Electrode selectivity

The error caused in the response of ISEs, due to the presence of interfering ion is usually described in terms of selectivity coefficients, K_{Sel} . In this work, the matched potential method (MPM) [67–69] was used for determination of selectivity coefficients. According to the method a known activity (concentration) of the target ions (A) is added to a reference solution and the potential is measured. In another test amounts of individual interfering ions (B) are gradually added to an identical reference solution, until the measured potential matches the one obtained before adding the primary ions. The MPM selectivity coefficient, K^{MPM} is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\text{MPM}} = \Delta a_A / a_B$.

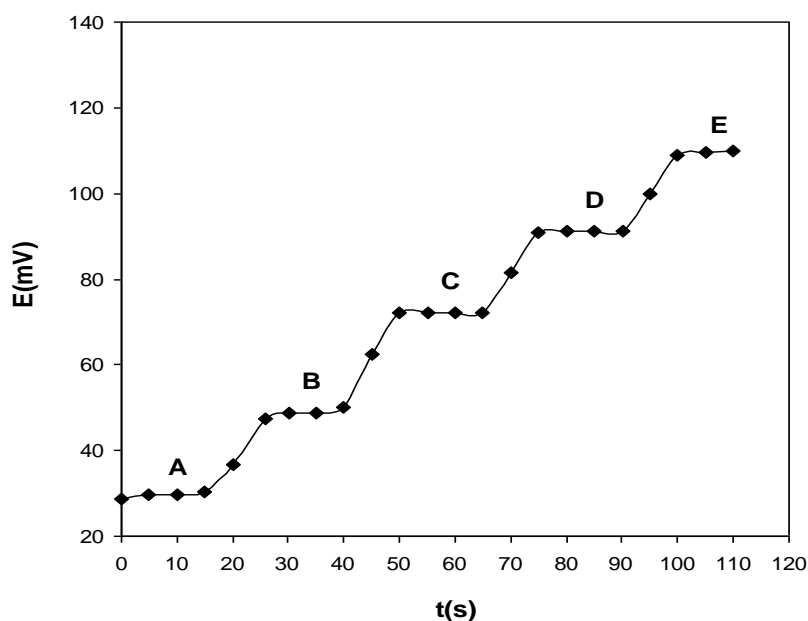


Figure 4. Dynamic response time of the terbium electrode (no. 6) for step changes in the Tb^{3+} concentration: A) $1.0 \times 10^{-6} \text{ mol L}^{-1}$, B) $1.0 \times 10^{-5} \text{ mol L}^{-1}$, C) $1.0 \times 10^{-4} \text{ mol L}^{-1}$, D) $1.0 \times 10^{-3} \text{ mol L}^{-1}$, E) $1.0 \times 10^{-2} \text{ mol L}^{-1}$.

The experimental conditions and the results are given in Table 2. As seen, for an ions used, the selectivity coefficients are in the order of 6.2×10^{-3} or smaller, showing they could not cause significant disturbances in the function of the electrode. Table 3 further compares the characterization of the sensor with those of three previously reported terbium sensors [70-72] and the results show a clear improvement in terms of selectivity coefficients, response time, and detection limits.

Table 2. Selectivity coefficients of the developed Tb^{3+} electrode

Ion	K^{MPM}
Nd^{3+}	3.2×10^{-3}
Sm^{3+}	6.8×10^{-4}
Lu^{3+}	7.7×10^{-4}
Gd^{3+}	2.3×10^{-3}
Pr^{3+}	8.5×10^{-4}
Eu^{3+}	4.6×10^{-3}
Cr^{3+}	2.1×10^{-3}
Pb^{2+}	8.3×10^{-4}
Cd^{2+}	6.2×10^{-3}
Ni^{2+}	4.8×10^{-3}
Co^{2+}	3.7×10^{-3}
Ca^{2+}	3.6×10^{-3}
Mg^{2+}	4.5×10^{-3}
Na^+	5.6×10^{-4}
K^+	4.3×10^{-4}

Table 3. Comparison of different Tb(III) electrodes

Parameter	Ref. 70	Ref. 71	Ref. 72	This work
LR (mol L ⁻¹)	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-5} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-2}
DL (mol L ⁻¹)	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	5.6×10^{-7}
Response time (s)	~10	15	<20	~10
pH range	3.5-8.0	3.8-8.2	3.5-7.7	2.8-8.5
Slope (mV/decade)	19.7	19.4	19.8	19.7
Log $K_{sel} > -2$	Gd	Gd	Ce, La, Dy, Yb, Sm	-

3.6. Analytical application

The proposed Tb(III) membrane electrode was found to work well under laboratory conditions and it was also successfully applied to the titration of 1.0×10^{-4} mol L⁻¹ Tb(III) solution with a standard 1.0×10^{-2} mol L⁻¹ EDTA solution (Fig. 5). As seen, the amount of Tb^{3+} in solution can be accurately determined with the electrode.

To validate the developed sensor, it was used in Tb^{3+} ion determination in terbium atomic

absorption standard solution (Aldrich Company; $1000 \mu\text{g L}^{-1}$ Tb in 1 wt.%HNO₃), as a certified reference material. It was found that Tb³⁺ concentration was satisfactory with the label amount ($1023 \pm 2.43 \mu\text{g L}^{-1}$).

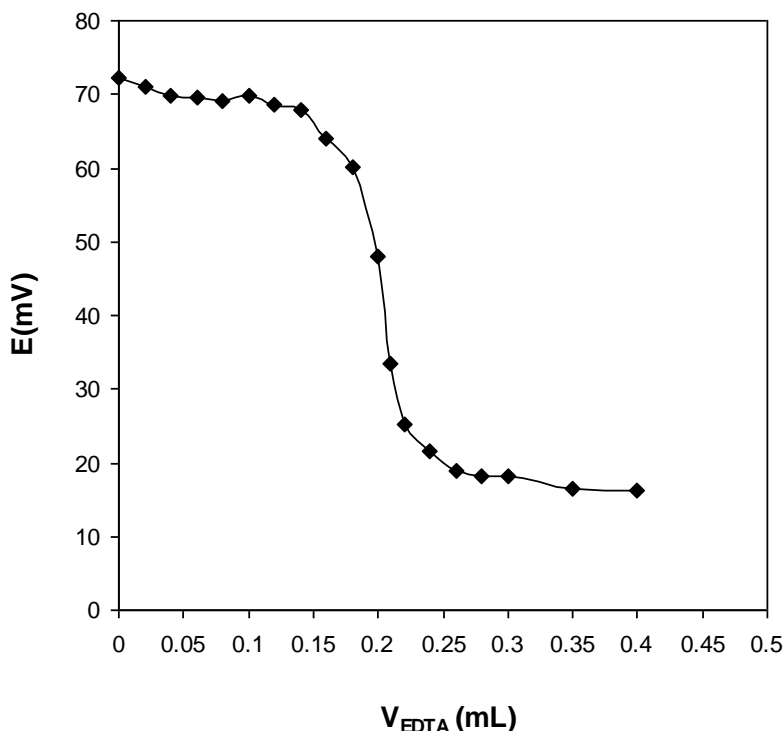


Figure 5. Potentiometric titration curve of 20.0 mL from a $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Tb³⁺ solution with $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of EDTA.

4. CONCLUSION

This study led to the introduction of an ion selective electrode, based on N-phenyl-2-(phenylcarbamothioyl) hydrazinecarboxamide (PPH), with enjoys the benefits low interference from common alkali, alkaline earth, transition and heavy metal ions, low detection limit, wide applicable pH range. The optimum membrane were found to have a composition of 3% PPH as ion carrier, 2% sodium tetraphenyl borate (NaTPB) as an anionic excluder, 65% dibutyl phthalate (DBP) as solvent mediator and 30% poly(vinyl chloride) (PVC) and the sensor was used for some applications to prove its robustness. Analysis of certified reference material confirmed the accuracy and precision of the proposed sensor.

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